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Thermal inkjet printing of thin-film electrolytes and buffering layers for solid oxide fuel cells with improved performance

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ABSTRACT

In this study, we report the facile fabrication of thin-film yttria-stabilized zirconia (YSZ) electrolytes and $Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC) buffering layers for solid oxide fuel cells (SOFCs) using a thermal inkjet printing technique. Stable YSZ and SDC inks with solids contents as high as 20 and 10 wt.%, respectively, were first prepared. One single printing typically resulted in an YSZ membrane with thickness of approximately 1.5 μm, and membranes with thicknesses varied from 1.5 to 7.5 μm were fabricated with multiple sequential printing. An as-fabricated cell with a $La_{0.8}Sr_{0.2}MnO_3$ (LSM) cathode delivered a peak power density (PPD) of 860 mW cm^{-2} at 800 °C. The SDC layer prepared using the inkjet printing method exhibited enclosed pores and a rough surface, which was, however, ideal for its application as a buffering layer. A cell with a dense 7.5-μm-thick YSZ layer, a 2-μm-thick SDC buffering layer and a $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) cathode was fabricated; this cell delivered a PPD of 1040 mW cm^{-2} at 750 °C and a high open circuit voltage (OCV) of approximately 1.10 V. The described technique provides a facile method for the fabrication of electrolytes for SOFCs with precise thickness control.

1. Introduction

The combination of elevated operation temperatures and all-solid components has made solid oxide fuel cells (SOFCs)—electrochemical energy conversion devices with high efficiency and low emissions—highly attractive for the generation of clean electrical power from a wide range of fuels. After intensive exploration over a period of several decades, it is generally accepted that the operating temperature of SOFCs should be reduced to an intermediate range of 500–800 °C to promote the commercialization of SOFC technology. Such a reduction would effectively reduce the cost and prolong lifetime of SOFCs, thus increasing their economic competitiveness with currently matured power generation technologies [1–3].

Since both the electrode reaction kinetics and the oxygen ion conductivity of the electrolyte are functions of the operating temperature because of their high activation energies, conventional SOFCs with thick yttria-stabilized zirconia (YSZ) electrolyte and $La_{0.8}Sr_{0.2}MnO_3$ (LSM) cathode usually show a sharp decrease in power output with decreased operating temperatures [4]. To maintain high power output at intermediate temperatures, strategies should be developed to reduce the cathodic polarization resistance as well as the electrolyte

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ohmic resistance of SOFCs [5–10]. With respect to the electrolyte, the ohmic resistance is a function of both the thickness and the ionic conductivity. The simplest way to reduce the ohmic resistance of an electrolyte membrane is to reduce its thickness. It was reported that the ohmic resistance of the state-of-the-art YSZ and $Ce_{0.9}Gd_{0.1}O_{1.95}$ (GDC) electrolytes can be controlled at a reasonable area-specific resistance of 0.15 Ω cm^2 at 700 and 500 °C, respectively, through a reduction of their thickness to approximately 15 μm [11]. Thus, the fabrication of thin-film electrolytes has become the main strategy to reduce the ohmic resistance for SOFCs operated at reduced temperatures [12–15].

Up to now, many technologies have been exploited for the fabrication of thin-film electrolytes for SOFCs, including chemical vapor deposition (CVD) and electrochemical vapor deposition (ECVD) [16], spray coating [17,18], electrophoretic deposition (EPD) [19,20], screen printing [21,22] and tape casting [23,24]. However, CVD and ECVD are not cost effective and are difficult to scale up, and tape casting and screen printing are difficult to use for the deposition of coatings with thicknesses less than 10 μm, although they are relatively inexpensive and commercially readily available processes.

Inkjet printing is widely used for texts and graphics output and is now being explored as a versatile manufacturing tool for applications in materials fabrication in areas such as electronics processing, ceramics, biological culture research, etc. [25–28]. Some attractive features of this technique include the simplicity of the devices involved, its low cost, the accurate control of features as well as high reproducibility. Inkjet printing is generally classified as continuous inkjet (CIJ) printing and drop-on-demand (DOD) inkjet printing [25,27]. Based on the printing mechanism, DOD printing can be divided into piezoelectric inkjet printing and thermal inkjet printing. The piezoelectric printers use a piezoelectric value to deliver the ink. Up to now, the majority of published works that involve inkjet printing technology for materials fabrication have reported using piezoelectric printing because of its simplicity in ink management. In the thermal inkjet printing process, a pulse of current is passed through the heating element to rapidly vaporize the ink to form a bubble, which causes a large pressure increase and forces a droplet of ink to deposit onto the substrate. The advantage of thermal inkjet printing is that the solid content in the ink can be high, which increases the print efficiency and significantly lowers the cost.

Recently, the inkjet printing method has also been used to fabricate thin-film electrolytes or cathodes for SOFCs [29–33]. Sukeshini et al. [29,30] have successfully fabricated dense YSZ electrolyte layers with a thickness of 6–12 μm for SOFCs using an inkjet printer and a YSZ ink with solid load of 5.64 wt.%. Peak power densities of 210 and 300 mW cm^{-2} at 800 °C were delivered for the cells with the LSM cathode layer deposited by hand painting and inkjet printing, respectively. Tomov et al. [31] also prepared dense YSZ electrolyte layer using a printer. Unlike Sukeshini et al., Tomov's group focused on the optimization of the YSZ ink and the working parameters of the inkjet printer, including the opening time of the orifice, the working pressure, etc. They successfully prepared a dense YSZ film with a thickness of 6 μm and believed that the electrolyte thickness could be further reduced through optimization of the printing procedure and suspension properties. Wang et al. [32] developed a sol-gel-based GDC precursor for deposition via inkjet printing. Using this precursor, they reduced the sintering temperature of the GDC electrolyte layer to 1100 °C. They believed the decreased sintering temperature can avoid long sintering time and excess sintering of the anode substrate. Recently, Yashiro et al. [33] successfully fabricated a $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSFC)–GDC cathode layer using the inkjet printing technique. Unfortunately, the performance of the cells that were prepared using the inkjet printing method was inferior to that of cells prepared using other methods, especially when it was applied for the electrolyte layer. These results suggest that their fabrication technique was not optimal.

In this study, we report the successful fabrication of thin-film electrolytes for SOFCs via a thermal inkjet printing method in which inks with a high solid content were used; the electrolytes are composed of YSZ with a $Ce_{0.8}Sm_{0.2}O_{1.9}$ (SDC) buffering layer. Both a high power density and a high open circuit voltage (OCV) were achieved. Our study proved the feasibility of the thermal inkjet printing as a technique for preparation of SOFCs.

2. Experimental

2.1. Powder synthesis

YSZ powder for the anode and SDC powder for buffering layer were synthesized via a co-precipitation method. As an example of the synthesis of YSZ, $ZrOCl_2 \cdot 8H_2O$ and $Y(NO_3)_3 \cdot 6H_2O$ were dissolved in de-ionized water with vigorous stirring; the molar ratio of Zr^{4+} and Y^{3+} corresponded to a formula of $(ZrO_2)_{0.92}(Y_2O_3)_{0.08}$. Ammonia was added as a precipitating agent until the pH was ~8; the obtained precipitate was collected via suction filtration and washed with water and ethanol 3 times. After the precipitate was dried at 110 °C for 24 h, it was subsequently fired at 700 °C for 2 h in air to produce the YSZ powder. The same procedure was used for the synthesis of SDC using $Ce(NO_3)_3 \cdot 6H_2O$ and $Sm(NO_3)_3 \cdot 6H_2O$ as raw materials and ammonium oxalate as the precipitating agent. All the raw materials used above were obtained from Sinopharm Chemical Reagent Co. Ltd., Shanghai, China in analytical grade.

2.2. Fabrication

2.2.1. Anode substrates

Anode substrates were fabricated using the tape-casting method. Nickel oxide (Chengdu Shudu Nano-Science Co. Ltd.) and YSZ (synthesized by the co-precipitation method) were mixed at a weight ratio of 6:4. Dimethylbenzene (Sinopharm Chemical Reagent Co. Ltd.) and ethanol were added as solvents, and fish oil (Sigma–Aldrich) was added as a dispersant. After the mixtures were ball milled for 24 h, some organic additives and PVB binder were added. Another 24 h of milling was performed to obtain slurry. Green anode supports were fabricated by tape-casting the slurry at a speed of 5 m min^{-1}, followed by drying in air for 12 h. Disk-shaped pellets were punched from the tape and sintered at 1100 °C for 2 h to serve as anode substrates.